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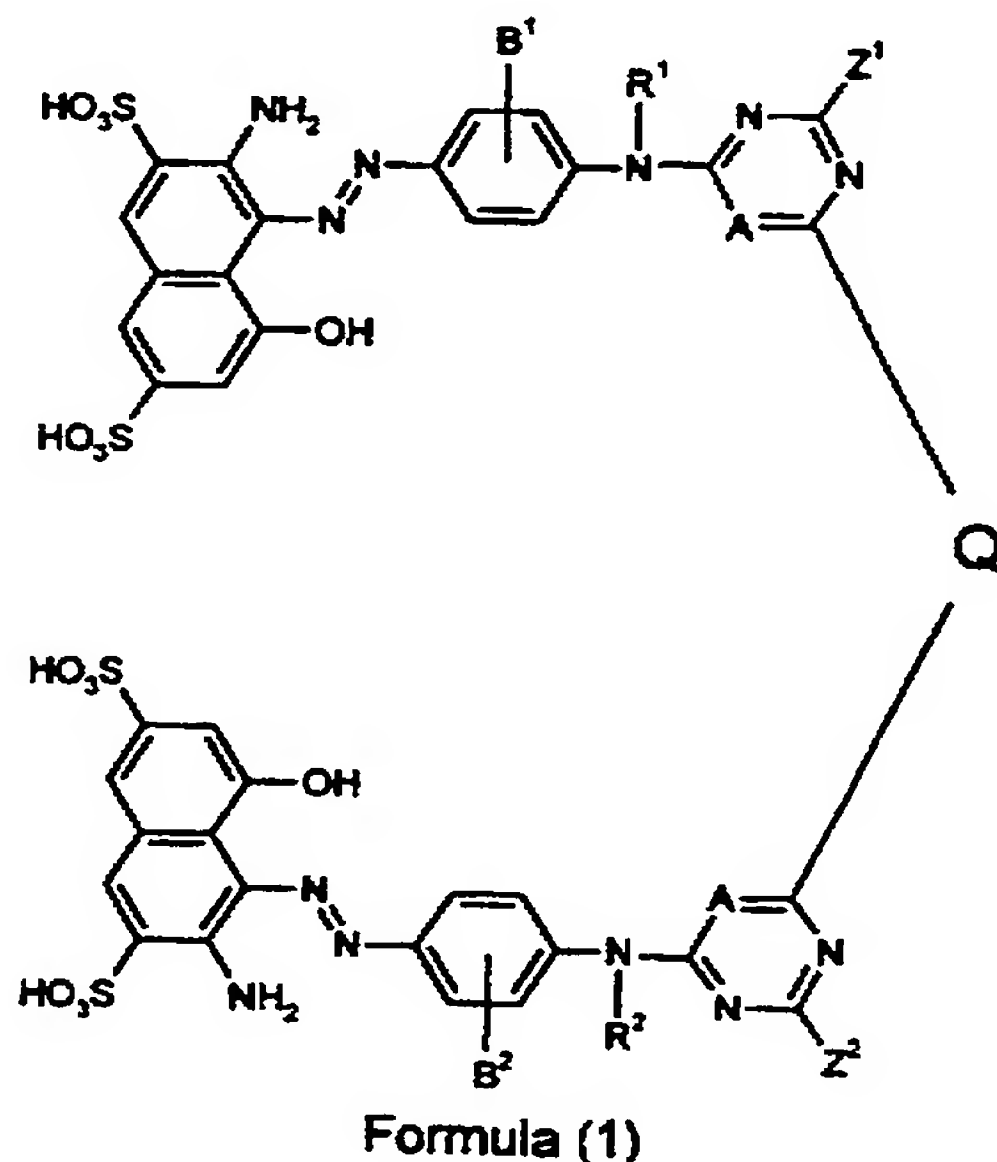
(58) Field of Search

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(54) Abstract Title

Bis[4-[2-amino-3,6-disulpho-8-hydroxynaphth-1-ylazo]anilino]- pyrimidinyl or 1,3,5-triazinyl] dyes & their use in ink jet printing inks

(57) Compounds of Formula (1) and salts thereof:



Formula (1)

[wherein:

B¹ and B²

are each independently -SO₃H, -COOH, -CF₃, optionally substituted alkoxy, optionally substituted alkyl or -PO₃H₂;

Q

is an organic linking group

R¹ and R²

are each independently H or optionally substituted alkyl;

each A

independently is N, C-Cl, C-CN or C-NO₂;

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Z^1 and Z^2 are each independently $-SR^3$, $-OR^4$, $-NR^5R^6$ or a labile atom or group [eg halogen; sulphonic acid, thiocyno, quaternary ammonium and pyridinium groups];
 R^3 , R^4 , R^5 and R^6 are each independently H, optionally substituted alkyl, optionally substituted aryl or optionally substituted aralkyl; or
 R^5 and R^6 together with the nitrogen to which they are attached form an optionally substituted five or six membered ring,]

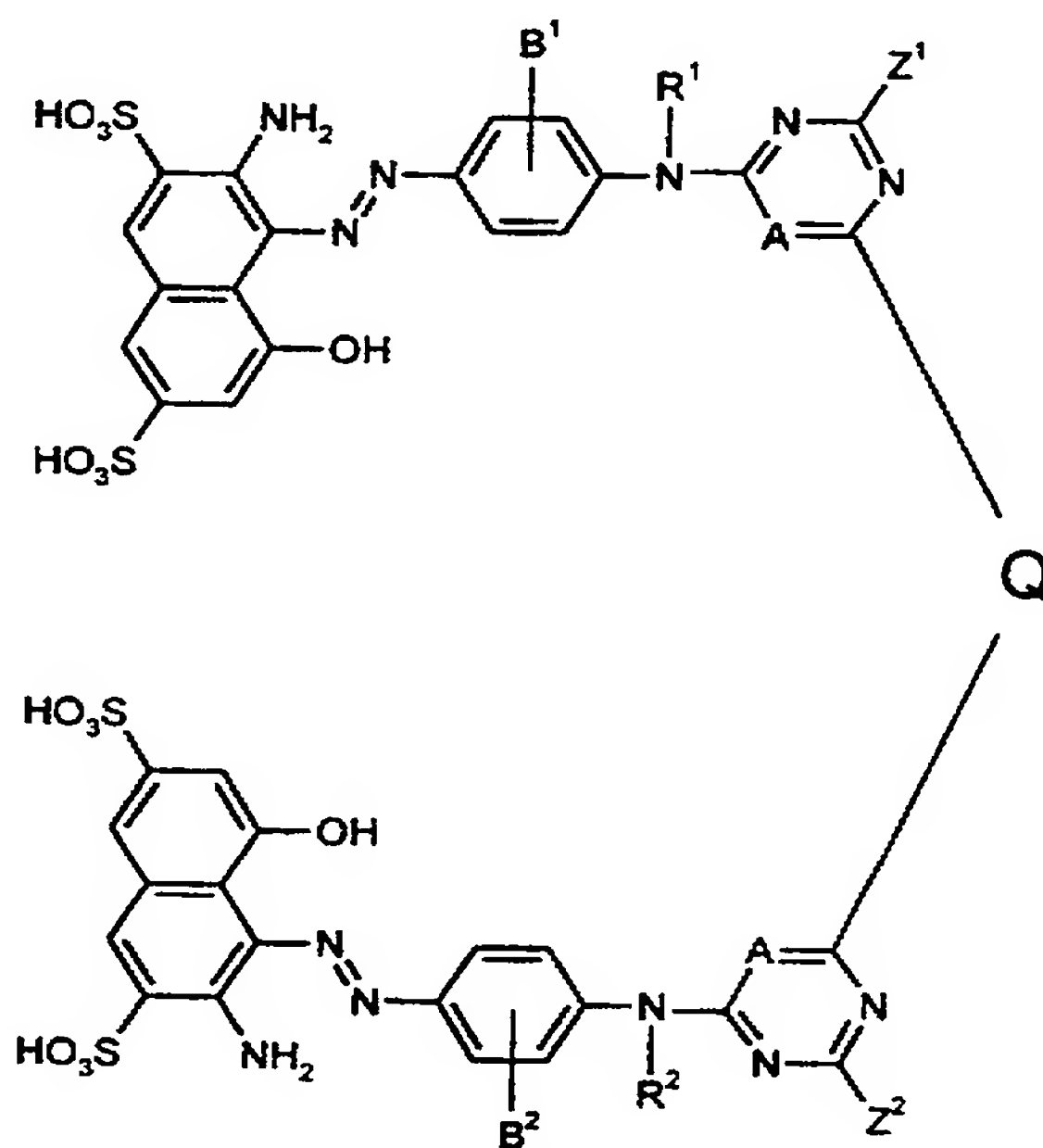
inks containing such compounds, an ink jet printing process using the inks, a substrate printed with the inks, and an ink jet printer cartridge containing an ink, wherein the ink contains one or more compound(s) of the Formula (1), are provided.

COMPOUNDS

This invention relates to dyes, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

According to the present invention there is provided a bis-azo compound of Formula (1) and salts thereof:



Formula (1)

wherein:

B¹ and B²

are each independently -SO₃H, -COOH, -CF₃, optionally substituted alkoxy, optionally substituted alkyl or -PO₃H₂;

Q

is an organic linking group;

R¹ and R²

are each independently H or optionally substituted alkyl;

each A

independently is N, C-Cl, C-CN or C-NO₂;

Z¹ and Z²

are each independently -SR³, -OR⁴, -NR⁵R⁶ or a labile atom or group;

R^3 , R^4 , R^5 and R^6 are each independently H, optionally substituted alkyl, optionally substituted aryl or optionally substituted aralkyl; or
 R^5 and R^6 together with the nitrogen to which they are attached form an optionally substituted five or six membered ring.

B^1 and B^2 are preferably attached ortho to the azo group. Preferably B^1 and B^2 are each independently $-SO_3H$, $-COOH$, $-CF_3$, alkoxy (preferably optionally substituted C_{1-4} -alkoxy), alkyl (preferably optionally substituted C_{1-4} -alkyl) or $-PO_3H_2$, more preferably $-SO_3H$, $-COOH$ or $-CF_3$ and especially $-SO_3H$. Preferred optional substituent(s) on B^1 or B^2 are selected from $-OH$, $-SO_3H$, $-COOH$, $-NH_2$, C_{1-4} -hydroxyalkyl, C_{1-4} -hydroxyalkoxy and C_{1-4} -alkoxy

Preferably each A is N.

Preferably R^1 and R^2 are each independently H or optionally substituted C_{1-4} -alkyl, more preferably H or C_{1-4} -alkyl optionally substituted by hydroxy, carboxy, sulpho or cyano. It is especially preferred that R^1 and R^2 are methyl or H, more especially H.

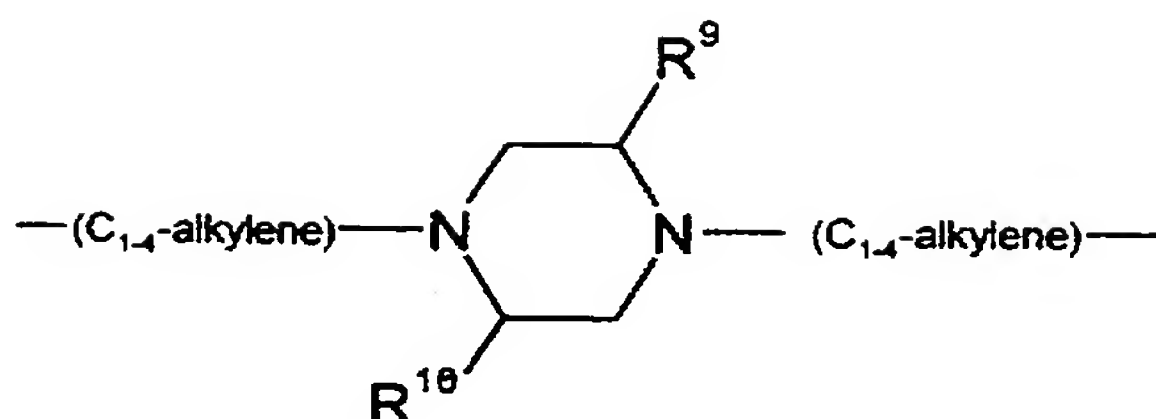
The organic linking group Q is preferably an optionally substituted piperazinylene group, or a group of the formula $-X^1-L-X^2-$ wherein X^1 and X^2 are each independently an optionally substituted piperazinylene group, $-S-$, $-O-$ or $-NR^7-$ wherein R^7 is H, optionally substituted alkyl or optionally substituted aryl, and L is a divalent organic linking group.

Preferred divalent organic linking groups represented by L are alkylene, preferably C_{1-20} -alkylene, more preferably C_{2-10} -alkylene, each of which is optionally interrupted; alkenylene, preferably C_{2-6} -alkenylene; arylene, preferably arylene containing up to ten carbon atoms, more preferably phenylene or naphthylene, especially 1,3-phenylene; aralkylene, more preferably C_{7-10} -aralkylene, especially phenylene- C_{1-6} -alkylene more especially $-phenylene-CH_2-$; and two arylene groups joined together either directly or through a vinyl, oxygen, nitrogen or sulphur link; each of the above divalent organic linking groups may be substituted or unsubstituted.

The optional substituent(s) on L are preferably selected from alkyl optionally substituted by hydroxy, carboxy or sulpho, preferably hydroxy- C_{1-4} -alkyl, carboxy- C_{1-4} -alkyl or sulpho- C_{1-4} -alkyl; alkoxy, preferably C_{1-4} -alkoxy and especially methoxy; phenyl optionally substituted by C_{1-4} -alkyl, carboxy, hydroxy, sulpho, cyano, amino or nitro; halo, preferably F or Cl; $-SO_3H$; $-COOH$; $-OH$; $-CN$; or $-NO_2$.

When L is an alkylene group it is preferably C_{2-10} -alkylene optionally interrupted by $-O-$; $-S-$; arylene, especially phenylene; $-NR^8-$; $-C(O)-$; $-C(O)O-$; or an optionally substituted piperazinylene group, wherein R^8 is H, C_{1-4} -alkyl, or $-C_{1-4}$ -hydroxyalkyl. When the interrupting group is optionally substituted piperazinylene it is preferably substituted by C_{1-6} -alkyl or C_{1-6} -alkyl substituted by hydroxy, carboxy or sulpho.

An especially preferred interrupted alkylene group is of the formula:



wherein:

R^9 and R^{10} each independently is H or C_{1-4} -alkyl optionally substituted by hydroxy, sulpho or carboxy.

5 Preferably R^9 and R^{10} are H.

Examples of optionally substituted alkylene groups represented by L include:

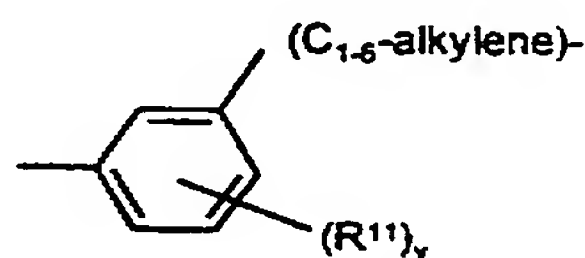
ethylene; 1,2- and 1,3-propylene; 2-hydroxy-1,3-propylene; 1,4-, 2,3- and 2,4-butylene; 2-methyl-1,3-propylene; 2-(4'-sulphophenyl)-1,3-propylene; 2-methyl-2,4-pentylene; 2,2-dimethyl-1,3-propylene; 1-chloro-2,3-propylene; 1,6- and 1,5-hexylene; 10 1-(methoxycarbonyl)-1,5-pentylene; 1-carboxy-1,5-pentylene; 2,7-heptylene; and 3-methyl-1,6-hexylene.

Examples of optionally interrupted alkylene groups represented by L include:

o-, m- and p-xylylene; $-CH_2CH=CHCH_2-$; $-CH_2CH_2OCH_2CH_2-$; $-CH_2CH_2SCH_2CH_2-$; $-CH_2NHCH_2-$ and



15 A preferred aralkyl group represented by L is of the Formula (2):



Formula (2)

wherein:

each R^{11} independently is H, C_{1-4} -alkoxy, F, Cl, $-SO_3H$, $-COOH$, $-OH$, $-CN$, $-NO_2$, $-NH_2$ or C_{1-4} -alkyl optionally substituted by hydroxy, carboxy or sulpho; and
25 y is 1 to 4.

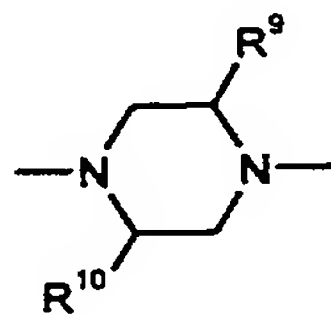
Preferably y is 1, 2 or 3, more preferably 1.

Examples of preferred arylene and aralkylene groups include $-C_6H_4-CH_2-$, $-C_6H_4-CH_2CH_2-$, 1,2-, 1,3- and 1,4-phenylene and 1,4-naphthylene.

When L is two arylene groups joined together directly it is preferably a biphenylene group, more preferably optionally substituted 4,4'-biphenylene.
30

When L is a two arylene groups joined by a divalent linking group it is preferably two of the hereinbefore defined arylene groups (especially optionally substituted phenylene) joined together by a linking group selected from -O-, -S-, -NR⁸-, -CH=CH- and C₂₋₆-alkylene optionally interrupted by -O-, -S- or -NR⁸-, wherein R⁸ is as hereinbefore defined. Examples of two arylene groups joined by a divalent linking group include diphen-4,4'-ylene-methane, -C₆H₄-CH₂CH₂-C₆H₄-, -C₆H₄-CH=CH-C₆H₄-, -C₆H₄-O-C₆H₄-, -C₆H₄-S-C₆H₄- and -C₆H₄-NHCH₂-C₆H₄-.

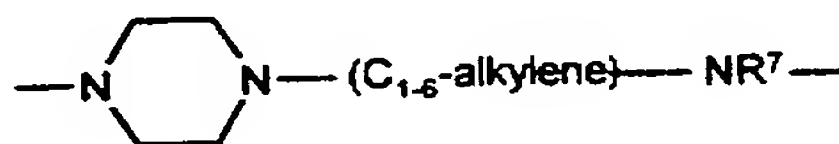
When Q, X¹ or X² is an optionally substituted piperazinylene group it is preferably of the Formula (3):



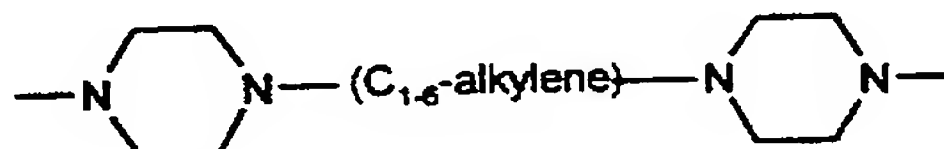
Formula (3)

wherein R⁹ and R¹⁰ are each independently as hereinbefore defined.

Preferred organic linking groups where one or both of X¹ and X² is an optionally substituted piperazinylene group are of the following formulae wherein R⁷ is as hereinbefore defined:



or



In a preferred embodiment Q is an optionally substituted piperazinylene group, or a group of the formula -X¹-L-X²- wherein X¹ and X² are each independently optionally substituted piperazinylene, -S- or -NR⁸- wherein R⁸ is as hereinbefore defined; and L is a group of Formula (2), 1,3-phenylene, or C₂₋₆-alkylene optionally interrupted by -O-, -S-, phenylene, -NR⁷-, -C(O)-, -C(O)O- or an optionally substituted piperazinylene group, wherein R⁷ is as hereinbefore defined. In this embodiment preferred optionally substituted piperazinylene groups are of Formula (3).

When Z¹ or Z² is a labile atom or group, it is preferably an atom or group which is displaceable by a hydroxyl group of cellulose under mildly alkaline aqueous conditions to form a covalent bond between the compound of Formula (1) and cellulose.

Preferred labile atoms and groups represented by Z¹ and Z² include halo, for example F and Cl; sulphonic acid groups; thiocyno groups; quaternary ammonium

groups, for example trialkylammonium groups and optionally substituted pyridinium groups, for example 3- and 4-carboxy pyridinium groups.

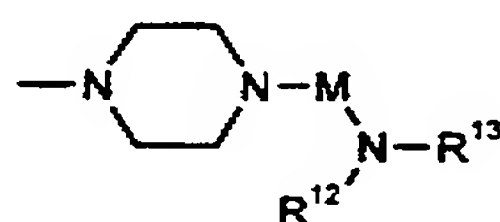
When R^3 , R^4 , R^5 , R^6 or R^7 is optionally substituted alkyl it is preferably optionally substituted C_{1-20} -alkyl, more preferably optionally substituted C_{1-10} -alkyl and especially optionally substituted C_{1-6} -alkyl. Preferred optional substituents include hydroxy, carboxy, sulpho, $-PO_3H_2$, cyano, a 5 or 6 membered heterocyclic group and optionally substituted amino. Preferred 5 or 6 membered heterocyclic groups are optionally substituted furanyl, tetrahydrofuranyl and morpholiny, more preferably furanyl and tetrahydrofuranyl optionally substituted by $-COOH$ or $-SO_3H$.

Preferred optionally substituted amino groups which may be present on R^3 , R^4 , R^5 and R^6 are of the formula $-NR^aR^b$ wherein R^a and R^b are each independently H; alkyl, more preferably C_{1-6} -alkyl, especially C_{1-4} -alkyl, more especially methyl, ethyl, n-propyl or iso-propyl; $-CO(alkyl)$, preferably $-CO(C_{1-6}-alkyl)$, more preferably $-CO(C_{1-4}-alkyl)$, especially $-COCH_3$, $-COCH_2CH_3$ and $-COCH_2CH_2CH_3$; or R^a and R^b together with the nitrogen to which they are attached form an optionally substituted morpholine, piperazine, piperidine or pyrrolidine ring.

When R^a and R^b together with the nitrogen to which they are attached form a substituted morpholine, piperazine, piperidine or pyrrolidine ring it preferably carries a substituent of the formula $-M-NR^{12}R^{13}$ wherein M is an alkylene linking group and R^{12} and R^{13} each independently is H or C_{1-6} -alkyl optionally substituted by hydroxy, C_{1-6} -alkoxy, sulpho or carboxy.

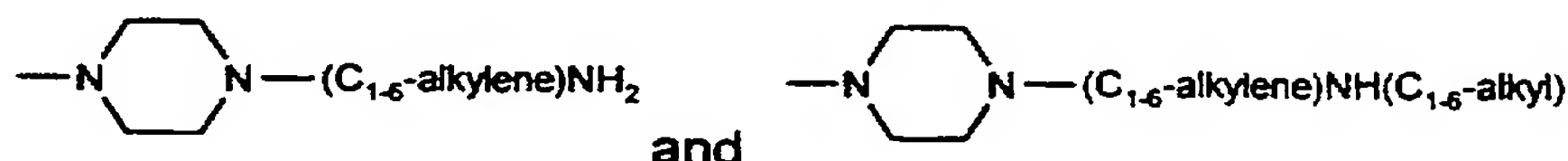
M is preferably C_{1-6} -alkylene, more preferably C_{2-6} -alkylene and especially $-(CH_2)_g-$, where g is from 2 to 6.

A preferred substituted piperaziny group represented by $-NR^aR^b$ is of the formula:



wherein M, R^{12} and R^{13} are as hereinbefore defined.

Especially preferred substituted piperaziny groups represented by $-NR^aR^b$ are of the formula:



A further preferred optionally substituted alkyl group represented by R^3 , R^4 , R^5 , R^6 or R^7 is of the Formula (4):



Formula (4)

wherein:

R^{14} is H or alkyl;
 5 a and b are different and from 1 to 6;
 p is from 1 to 4; and
 q is from 0 to 3.

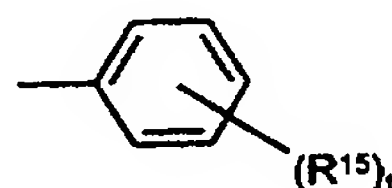
Preferably R^{14} is H or C_{1-4} -alkyl, more preferably H.

10 Preferably a and b are each independently 2 to 6, more preferably 2 or 3. p is preferably 1 or 2. Preferably q is 0.

Preferred groups of the Formula (4) are of the formula
 $-(C_{1-6}\text{-alkylene})O(C_{1-6}\text{-alkylene})OC_{1-4}\text{alkyl}$ or $-(C_{2-6}\text{-alkylene})O(C_{2-6}\text{-alkylene})OH$. Examples
 of such groups include $-C_2H_4OC_2H_4OH$, $-C_2H_4OC_2H_4OCH_3$, $-CH_2CH(CH_3)CH_2OC_2H_4OH$
 and

15 $-C_3H_6OC_2H_4OH$.

When R^3 , R^4 , R^5 , R^6 or R^7 is optionally substituted aryl it is preferably optionally
 substituted phenyl or naphthyl, more preferably optionally substituted phenyl. Preferred
 optional substituents are C_{1-6} -alkoxy, C_{1-6} -alkyl, C_{1-6} -alkyl substituted by hydroxy, carboxy
 or sulpho, halo (preferably F or Cl), hydroxy, cyano, carboxy, sulpho, $-PO_3H_2$, nitro,
 20 amino, $-COC_{1-4}\text{-alkyl}$, $-NHCOC_{1-4}\text{-alkyl}$, $-SO_2NH_2$ and $-SO_2NHCOC_{1-4}\text{-alkyl}$. More
 preferably the optionally substituted aryl group is of the formula:



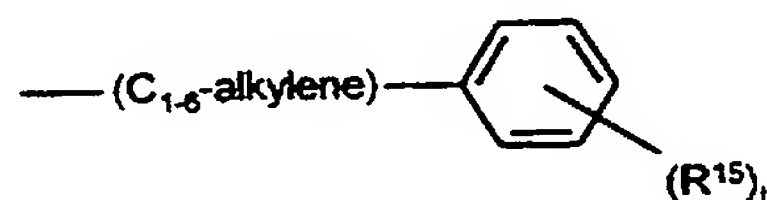
wherein:

25 R^{15} is C_{1-4} -alkyl, C_{1-4} -alkoxy, halo, hydroxy, carboxy, sulpho or $-PO_3H_2$; and
 t is 0 to 5.

t is preferably 0, 1 or 2.

When R^3 , R^4 , R^5 or R^6 is optionally substituted aralkyl it is preferably of the
 formula:

30



wherein R^{15} and t are as hereinbefore defined.

When R^5 and R^6 together with the nitrogen to which they are attached form an
 optionally substituted 5 or 6 membered ring it is preferably an optionally substituted
 35 piperazine, piperidine, pyrrolidine or morpholine ring. The substituents are preferably
 selected from hydroxy, carboxy, sulpho, C_{1-6} -alkoxy, C_{1-6} -alkyl and C_{1-6} -alkyl substituted by

hydroxy, carboxy, sulpho and optionally substituted amino as hereinbefore defined. An especially preferred optional substituent is $-M-NR^{12}R^{13}$ wherein R^{12} and R^{13} are as hereinbefore defined.

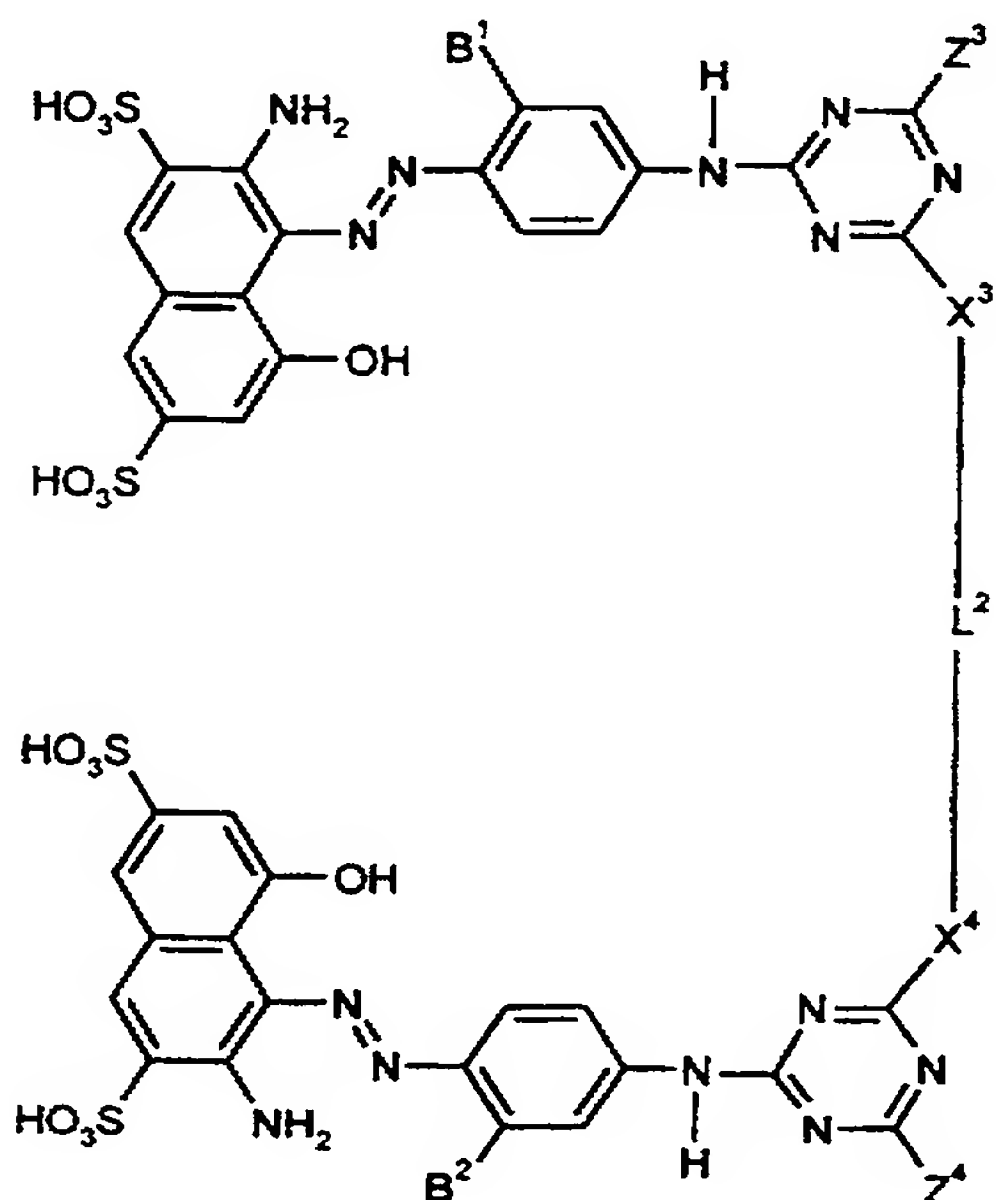
5 Preferably R^7 is H or C_{1-4} -alkyl optionally substituted by hydroxy, carboxy or sulpho.

R^4 is preferably H or C_{1-4} -alkyl.

Preferably Z^1 and Z^2 are each independently halo, more preferably $-SR^3$, $-OR^4$ or $-NR^5R^6$, especially $-SR^3$ or $-NR^5R^6$, more especially $-SR^3$ or $-NHR^5$, wherein R^3 , R^4 , R^5 and R^6 are as hereinbefore defined.

10 The compound of Formula (1) preferably contains only two azo groups ($-N=N-$).

In view of the foregoing preferences, preferred compounds of the Formula (1) are bis-azo compounds of the Formula (5) and salts thereof:



Formula (5)

wherein:

X^3 and X^4 are each independently an optionally substituted piperazinylene group, $-S-$ or a group of formula $-NR^7-$;

20 L^2 is optionally substituted phenylene, a group of the Formula (2) as hereinbefore defined, or C_{2-6} -alkylene optionally interrupted by $-O-$, $-S-$, phenylene, $-NR^7-$, $-C(O)-$, $-C(O)O-$ or an optionally substituted piperazinylene group; or

$-X^3L^2X^4-$ forms an optionally substituted piperazinylene group;

25 Z^3 and Z^4 are each independently Cl, F, $-SR^3$, $-OR^4$ or $-NR^5R^6$; and

B^1 , B^2 , R^3 , R^4 , R^5 , R^6 and R^7 are as hereinbefore defined.

The optionally substituted piperazinylene groups referred to in the definitions of X^3 , X^4 , L^2 and $-X^3L^2X^4-$ are preferably of Formula (3), as hereinbefore defined.

Z^3 and Z^4 are preferably each independently $-SR^3$, $-OR^4$ or $-NR^5R^6$, wherein R^3 , R^4 , R^5 and R^6 are as hereinbefore defined.

A particularly preferred embodiment of the present invention comprises a compound of Formula (5) and salts thereof wherein :

X^3 and X^4 are each independently $-NR^8-$ or $-S-$;

Z^3 and Z^4 are each independently $-SR^{16}$ or $-NR^{17}R^{18}$;

R^{16} and R^{17} are each independently a group of the formula

$-(C_{1-6}\text{-alkylene})O(C_{1-6}\text{-alkylene})OR^{19}$ or $C_{1-6}\text{-alkyl}$ optionally substituted by $C_{1-4}\text{-alkoxy}$, hydroxy, carboxy, sulpho, tetrahydrofuryl, morpholinyl or a group of the formula $-NR^{19}CO(C_{1-4}\text{-alkyl})$;

R^{18} and R^{19} are each independently H or $C_{1-4}\text{-alkyl}$ or $C_{1-4}\text{-hydroxyalkyl}$;

B^1 and B^2 are sulpho; and

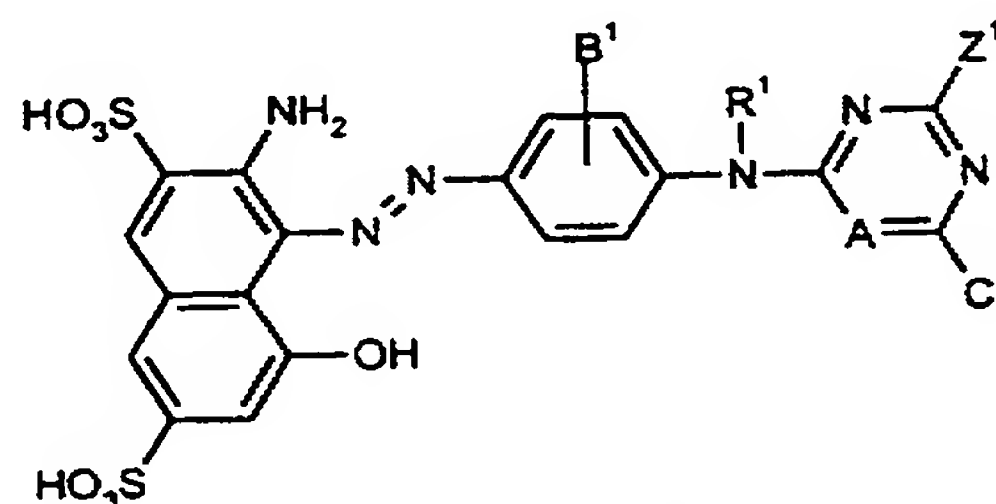
L^2 and R^8 are as hereinbefore defined.

Preferably L^2 is $C_{2-10}\text{-alkylene}$ optionally interrupted by $-NR^8-$ wherein R^8 is as hereinbefore defined.

For ease of synthesis B^1 and B^2 are preferably the same and Z^1 and Z^2 are the same.

The compounds of the invention may be in the free acid or salt form. Preferred salts are water-soluble, for example alkali metal salts, especially lithium, sodium and potassium salts, ammonium and substituted ammonium salts. Especially preferred salts are salts with sodium, lithium, ammonia and volatile amines. The compounds may be converted into a salt using known techniques. For example, an alkali metal salt of a compound may be converted into a salt with ammonia or an amine by dissolving an alkali metal salt of the compound in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal cations by dialysis, reverse osmosis or ultrafiltration.

The compounds of the invention may be prepared using conventional techniques for the preparation of azo dyes. For example a suitable method comprises condensing a compound of the Formula HQH with approximately 2 molar equivalents of a compound of the Formula (6):



Formula (6)

wherein Q, B, R¹ and Z¹ are as hereinbefore defined.

The compound HQH is preferably of the formula HX¹LX²H wherein X¹, X² and L are as hereinbefore defined.

5 The condensation is preferably performed in a liquid medium, more preferably an aqueous medium and especially water. Temperatures of 15°C to 100°C are preferred, more preferably from 30 to 40°C. Preferably a reaction time of 1 to 48, more preferably 3 to 24 hours is used.

10 The condensation is preferably performed in the presence of a base. The base may be any inorganic base for example, ammonia, an alkali metal or alkali earth metal hydroxide, carbonate or bicarbonate, or an organic base. Preferred organic bases are tertiary amines for example, N-alkylated heterocycles, for example N-(C₁₋₄-alkyl)morpholine, N-(C₁₋₄-alkyl)piperidine, N,N'-di(C₁₋₄-alkyl)piperazine; tri(C₁₋₄-alkyl)amines, for example triethylamine, and optionally substituted pyridines, especially pyridine.

15 The amount of base used may be varied between wide limits but it is preferred to use less than 40, more preferably less than 10 and especially from 3 to 5 moles for each mole of the compound of Formula (6).

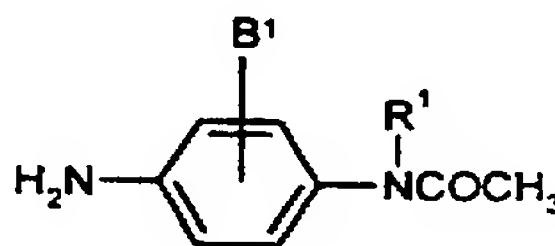
20 After the condensation the product may be isolated by precipitating the product as a salt from the reaction mixture for example by the addition of a suitable alkali metal salt, especially sodium chloride. Alternatively, the product may be isolated in its free acid form by acidifying the reaction mixture, preferably using a mineral acid, especially hydrochloric acid. Where the product precipitates as a solid it may be separated from the mixture by filtration.

25 If desired unwanted anions may be removed from the product of the above process by dialysis, osmosis, ultrafiltration or a combination thereof.

30 The product of the above process may be converted, if desired, to the NH₄⁺, quaternary ammonium or organic amine salt by the addition of ammonia, ammonium hydroxide, primary, secondary, tertiary or quaternary amine. When the base used in the condensation process is an organic amine an excess may be used so that the compound of Formula (1) is formed as the organic amine salt.

The compound of the Formula (6) may be prepared using conventional techniques, for example by:

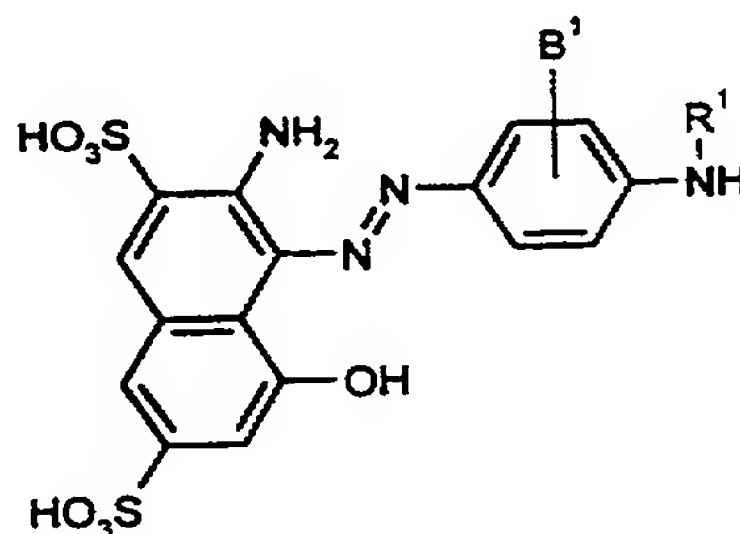
- (1) diazotising a compound of the Formula (7) to give the corresponding diazonium salt:



Formula (7)

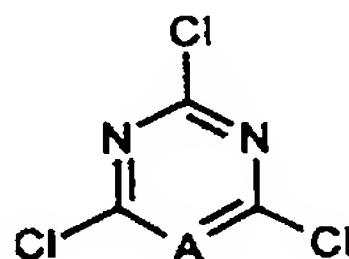
wherein R^1 and B^1 is as hereinbefore defined;

- (2) coupling the diazonium salt from stage (1) with 2-amino-8-naphthol-3,6-disulphonic acid at a pH < 7, preferably at a pH of from 3 to 5;
- (3) hydrolysing the product of stage (2) under alkaline conditions to give a compound of the Formula (8):



Formula (8)

- (4) condensing the product from stage (3) with approximately 1 molar equivalent of the compound of the formula:



- wherein A is as hereinbefore defined; and
- (5) condensing the product from stage (4) with approximately 1 molar equivalent of the compound of the formula Z^1H .

The diazotisation in stage (1) is preferably performed in an aqueous medium at a pH below 7 in the presence of a suitable diazotisation agent. Dilute mineral acid, e.g. HCl or H_2SO_4 , is preferably used to achieve the desired acidic conditions. Conveniently the diazotisation agent is formed in-situ, for example by dissolving an alkali metal nitrite, preferably sodium nitrite, in a molar excess of mineral acid, preferably HCl. Normally at least one mole of diazotisation agent per mole of the compound of Formula (7), preferably from 1 to 1.25 moles will be used in the diazotisation.

The temperature of the diazotisation is not critical and may conveniently be carried out at from $-5^\circ C$ to $20^\circ C$, preferably from 0 to $10^\circ C$ and especially from 0 to $5^\circ C$.

The hydrolysis in stage (3) is preferably performed at a pH of from 9 to 14. The temperature during hydrolysis is preferably 40 to $90^\circ C$.

When B^1 and B^2 , R^1 and R^2 or Z^1 and Z^2 are different, the compounds of Formula (1) are preferably prepared by condensing a compound of the Formula (6) with an approximately equimolar quantity of the compound of the formula HQH (preferably HX^1LX^2H). The product of this reaction is then further condensed with an approximately

equimolar quantity of a compound of the Formula (6) wherein R^1 is R^2 , B^1 is B^2 and Z^1 is Z^2 as hereinbefore defined.

Alternatively, a compound of Formula (1) or Formula (5) in which one or both of Z^1 and Z^2 are other than halogen, may be prepared by condensing a compound of Formula (1) or Formula (5), in which $Z^1 = Z^2 = Cl$, with sufficient of a compound or compounds Z^1H and/or Z^2H , wherein Z^1 and Z^2 are as hereinbefore defined except for Cl , under such conditions of temperature and/or time as to replace one or both Cl atoms.

The compounds according to the present invention may be, and preferably are, purified to remove undesirable impurities before they are incorporated into inks for ink jet printing. Conventional techniques may be employed for purifying the dyes, for example ultrafiltration, reverse osmosis and/or dialysis.

The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present claims.

The compounds of Formula (1) are useful as dyes, especially for the coloration of inks for ink jet printing. The compounds exhibit a high solubility in aqueous media and provide prints which exhibit high light-fastness and water-fastness when incorporated into inks for ink jet printing.

According to a second aspect of the present invention there is provided a composition comprising one or more compound(s) of the Formula (1) (more preferably Formula (5)) or a salt thereof and a medium.

The compositions according to the second aspect of the invention are useful as inks, particularly printing inks and especially ink jet printing inks.

The medium is preferably water, a mixture of water and an organic solvent, an organic solvent free from water, or a low melting point solid.

A preferred composition comprises:

- (a) from 0.01 to 30 parts of one or more compound(s) of the Formula (1) or (5) or salt thereof as hereinbefore defined; and
- (b) from 70 to 99.99 parts of a medium comprising a mixture of water and an organic solvent, an organic solvent free from water, or a low melting point solid;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

When the medium is a mixture of water and an organic solvent or an organic solvent free from water, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks

and reduces the chance of the compound of Formula (1) precipitating if evaporation of the liquid medium occurs during storage.

When the medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

A preferred medium comprises:

- (a) from 75 to 95 parts water; and
- (b) from 25 to 5 parts in total of one or more solvents selected from diethylene glycol, 2-pyrrolidone, thiodiglycol, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam and pentane-1,5-diol;

wherein the parts are by weight and the sum of the parts (a) and (b) = 100.

Examples of further suitable media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH_2Cl_2 ; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C_{1-4} -alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C_{1-4} -alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the composition.

Media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C_{18-24} chains, and sulphonamides. The compound of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

The compounds according to the present invention exhibit a high solubility in aqueous media, accordingly it is preferred that the liquid medium is water or more preferably a mixture of water and one or more water miscible organic solvent(s).

The composition may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogation reducing additives and surfactants which may be ionic or non-ionic.

When a composition according to the second aspect of the present invention is used as an ink jet printing ink, the ink preferably has a concentration of less than 100 parts per million, more preferably less than 50 parts per million, in total of halide ions and divalent and trivalent metals. This reduces nozzle blockage in ink jet printing heads, particularly in thermal ink jet printers.

A third aspect of the present invention provides a process for printing an image on a substrate comprising applying thereto an ink containing a compound of Formula (1) by means of an ink jet printer.

The ink used in this process preferably comprises a composition as defined in the second aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available treated papers include HP Premium Coated Paper (available from Hewlett Packard Inc), HP Photopaper (available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film (available from Seiko Epson Corp.), Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper (available from Canon), Canon GP 201 Glossy Paper (available from Canon), and Canon HG 101 High Gloss Film (available from Canon).

A fourth aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with a composition according to the second aspect of the present invention or by means of the process according to the third aspect of the present invention.

When the substrate is a textile material the ink according to the invention is preferably applied thereto by:

- i) applying the composition to the textile material using an ink jet printer, and
- ii) heating the printed textile material at a temperature of from 50°C to 250°C.

Preferred textile materials are natural, synthetic and semi-synthetic materials. Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and semi-synthetic materials include polyamides, polyesters, polyacrylonitriles and polyurethanes.

Preferably the textile material has been treated with an aqueous pre-treatment composition comprising a thickening agent and optionally a water-soluble base and a hydrotropic agent and dried prior to step i) above.

The pre-treatment composition preferably comprises a solution of the base and the hydrotropic agent in water containing the thickening agent. Particularly preferred pre-treatment compositions are described more fully in European Patent Application No.534660A1.

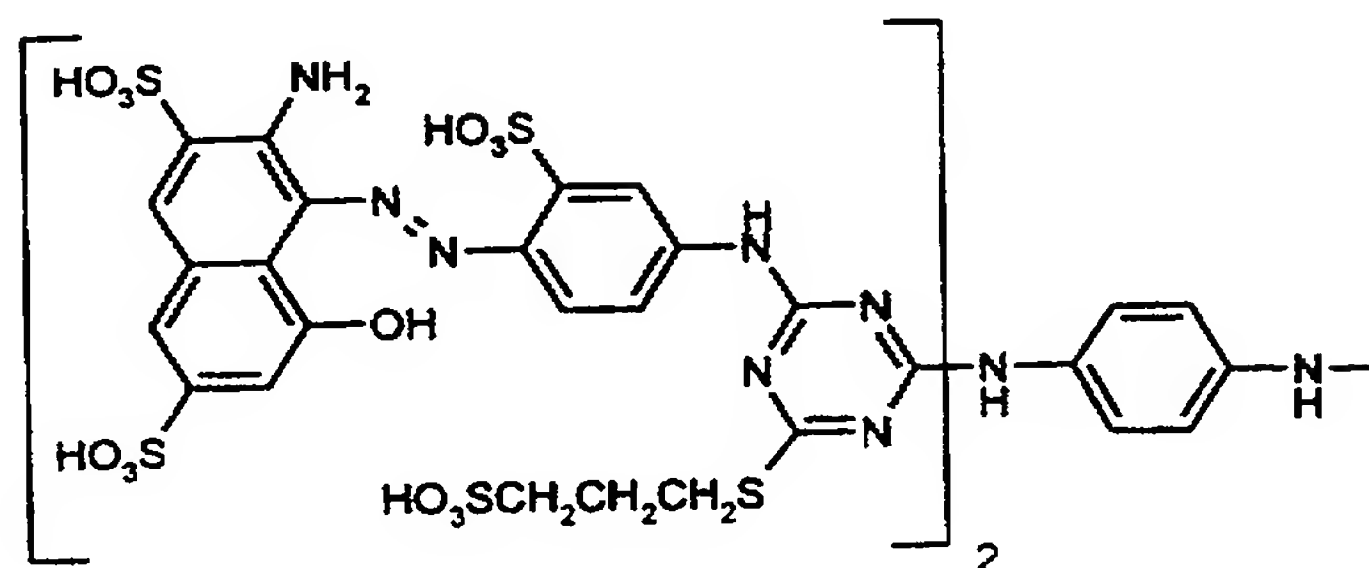
5 According to a fifth aspect of the present invention there is provided an ink jet printer cartridge containing an ink, characterised in that the ink contains one or more compound(s) of the Formula (1) or salts thereof as defined in the first aspect of the invention.

 Preferably the ink contained in the ink jet printer cartridge is an ink according to the second aspect of the present invention.

10 The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1**Dye**

Dye (1) was prepared using the process described below :



Dye (1)

Stage (1) : Diazotisation and Coupling

To N-acetyl *p*-phenylenediamine sulphonic acid (0.5moles) in water (400ml) was added concentrated hydrochloric acid (250ml) and the solution was cooled to 0-5°C. 2N sodium nitrite (250ml) was added dropwise over 5 minutes with stirring. After 15 minutes, excess nitrous acid was destroyed by the addition of sulphamic acid (0.2g). To the resulting suspension was added a solution of 2-amino-8-naphthol-3,6-disulphonic acid (0.5 moles in 600ml of water at pH6) and the pH was adjusted to 4 by the addition of sodium acetate. The mixture was stirred at 0-5°C for 4 hours before being allowed to warm to room temperature.

Stage (ii) Hydrolysis

The acetyl group present on the product of stage (i) was removed by alkaline hydrolysis by adding concentrated sodium hydroxide (200ml) to the mixture resulting from stage 1 and heating at 70-80°C for 1.5 hours.

After cooling to room temperature, the pH was adjusted to 7 by the addition of concentrated hydrochloric acid. Sodium chloride (20% weight/volume) was added and the precipitated solid was collected by suction filtration, washed with 30% brine and dried at 70°C. Yield 197g (strength 49%).

Stage (iii) Condensation with Cyanuric Chloride

The product from stage (ii) (17.3g) was dissolved in water (400ml) at pH7 and cooled to 0-5°C. Cyanuric chloride (3.7g) in acetone (100ml) was added dropwise with stirring over a period of 30 minutes and the mixture was stirred for a further ½ hour.

Stage (iv) Condensations

p-Phenylene diamine (1g) was added followed by N-methyl pyrrolidone (100ml) and the mixture was stirred at 30°C for 4 hours.

Mercaptopropane sulphonic acid (12g) was added and the mixture was warmed to 70-80°C for 4 hours. After cooling, methylated spirits (400ml) was added and the precipitated product was collected by suction filtration. The solid was washed with methylated spirits/water (2:1; 200ml). The dye was re-dissolved in deionized water (400ml) and dialysed using Visking tubing to a permeate conductivity of below 100 μ S.

Stage (v) Purification

The product of stage (iv) was re-dissolved in distilled water and dialysed using Visking tubing to a permeate conductivity of below 100 μ S. Yield 10.8g.

Ink

Ink I was prepared by dissolving 2 parts of Dye (1) in 98 parts of a mixture comprising 90 parts water and 10 parts 2-pyrrolidone.

Ink Jet Printing

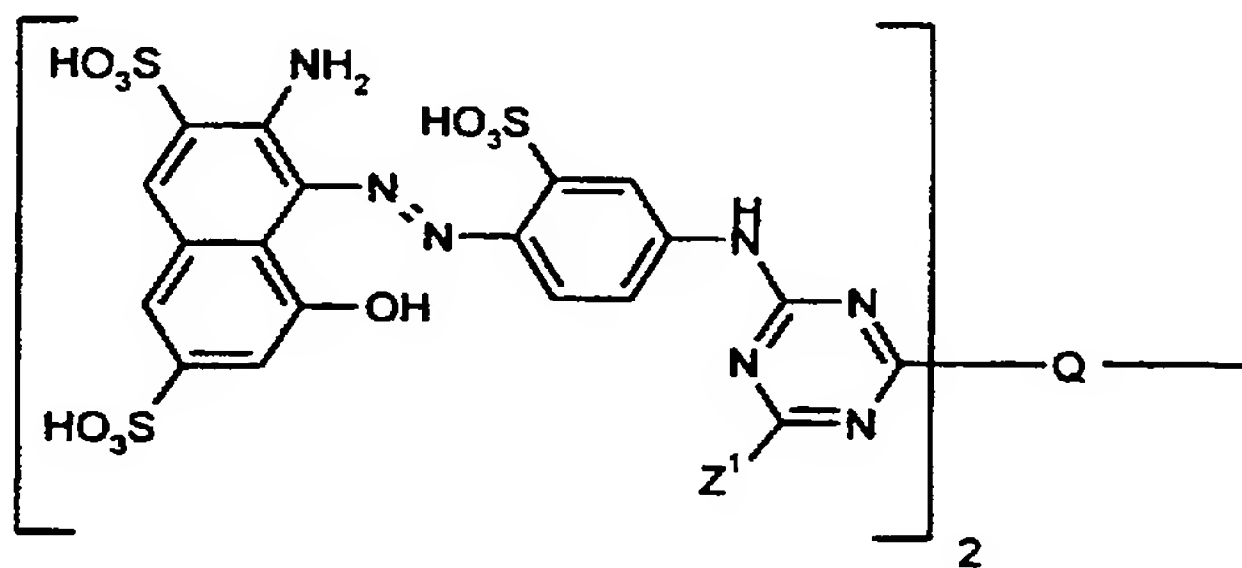
Ink I was loaded into an HP 660C ink jet printer and was printed onto HP Premium Glossy Paper (available from Hewlett Packard Inc.). The resulting print was a bright magenta which had a good optical density and excellent light fastness.

The optical density of the print was 1.67, as measured by an X-Rite densitometer.

The print exhibited a ΔE value of 3.3, as measured by X-Rite Densitometer, and an optical density loss of 9% after 64 hours irradiation in the Atlas Weatherometer.

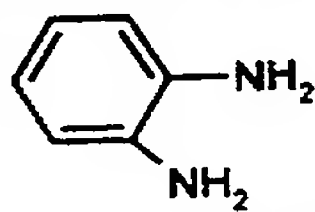
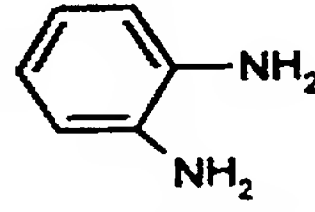
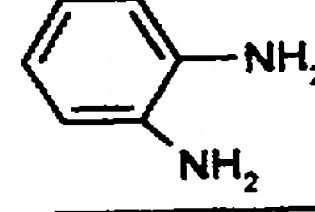
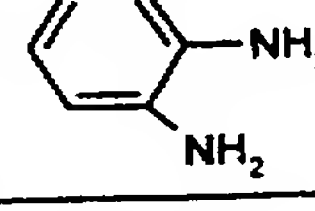
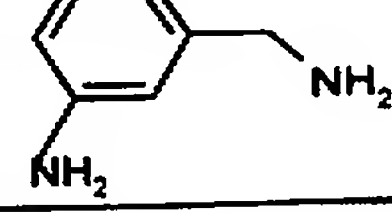
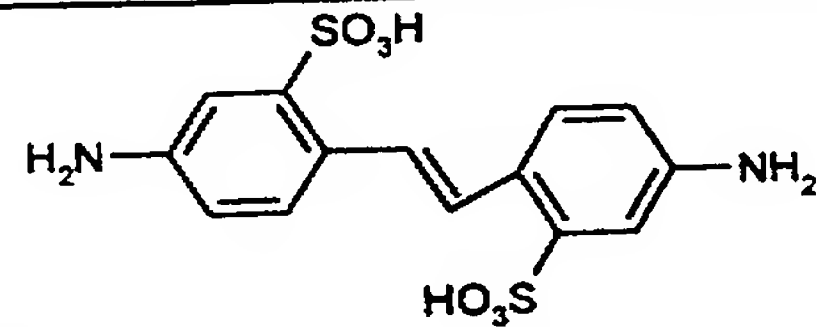
Example 2

Dyes of the formula:



were prepared by condensing the compound H-Q-H shown in Table 1 with approximately 2 molar equivalents of the product of stage (iii) in Example 1. The resulting product was then condensed with approximately 2 molar equivalents of the compound of the formula Z'H shown in Table 1. The reaction conditions used were analogous to those used in stage (iv) of Example 1. In Table 1 the symbol "-" indicates that the compound was not condensed with Z'H, i.e. Z' = -Cl.

Table 1

Dye	HQH	Z'H
2	$\text{H}_2\text{N}(\text{CH}_2)_3(\text{O}(\text{CH}_2)_2)_2\text{O}(\text{CH}_2)_3\text{NH}_2$	$\text{SH}(\text{CH}_2)_3\text{SO}_3\text{H}$
3	$\text{H}_2\text{N}(\text{CH}_2)_3(\text{O}(\text{CH}_2)_2)_2\text{O}(\text{CH}_2)_3\text{NH}_2$	$\text{SH}(\text{CH}_2)_2\text{COOH}$
4	$\text{H}_2\text{N}(\text{CH}_2)_3(\text{O}(\text{CH}_2)_2)_2\text{O}(\text{CH}_2)_3\text{NH}_2$	$\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$
5		-
6		$\text{SH}(\text{CH}_2)_2\text{COOH}$
7		$\text{SH}(\text{CH}_2)_3\text{SO}_3\text{H}$
8		$\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$
9		$\text{SH}(\text{CH}_2)_2\text{COOH}$
10	$\text{H}_2\text{N}(\text{CH}_2)_3(\text{O}(\text{CH}_2)_2)_2\text{O}(\text{CH}_2)_3\text{NH}_2$	$\text{NH}_2(\text{CH}_2)_5\text{OH}$
11	$\text{H}_2\text{N}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{NH}_2$	$\text{SHCH}(\text{CH}_3)\text{COOH}$
12		$\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$
13	$\text{HS}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{SH}$	$\text{H}_2\text{N}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$
14	$\text{HS}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{SH}$	$\text{NH}_2(\text{CH}_2)_9\text{CH}_3$

Example 3 Inks

5

The inks described in Tables 2 and 3 may be prepared wherein the Dye described in the first column is the Dye made in Examples 1 and 2 of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

10

The following abbreviations are used in Table 2 and 3:

PG = propylene glycol

PHO = Na_2HPO_4

TBT = tertiary butanol

BDL = butane-2,3-diol

TDG = thiodiglycol

CET = cetyl ammonium bromide

5

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

2P = 2-pyrrolidone

10

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

TABLE 2

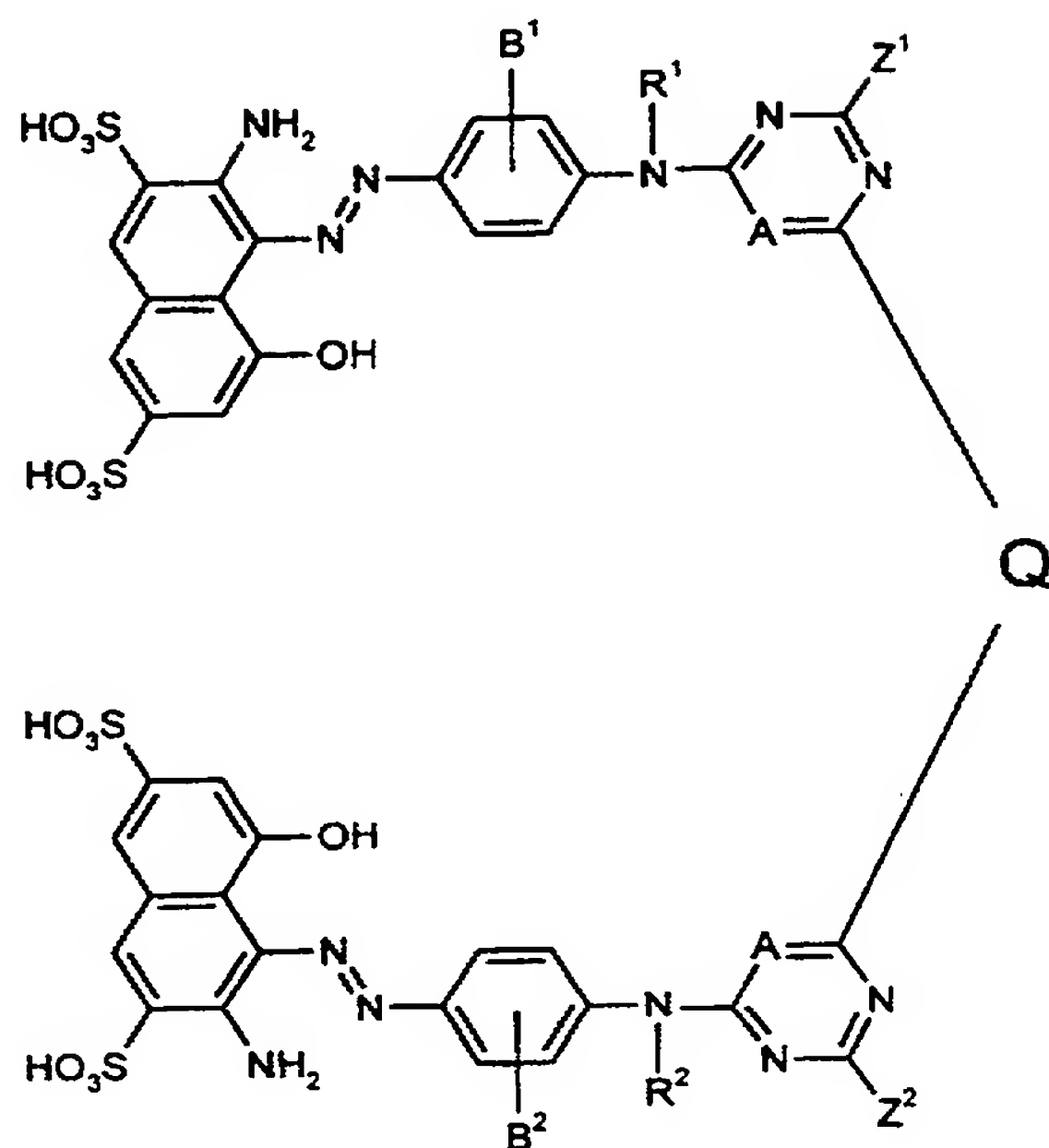
Dye	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2			5	1	
3	10.0	85	3	8	3	3						1
4	2.1	91						0.2	4			5
5	3.1	86	5				0.5	0.5			9	
6	1.1	81			9	3			6	10	5	4
7	2.5	60	4	15	3	3			10			
8	5	65		20		5				6		5
9	2.4	75	5	4								
10	4.1	80	3	5	2	10		0.3			6	5
11	3.2	65		5	4	6			5	4		
12	5.1	96							5	4		
13	10.8	90	5						1		4	
14	10.0	80	2	6	2	5					15	
10	1.8	80		5							5	
9	2.6	84			11					2		6
6	3.3	80	2			10			3			
5	12.0	90				7	0.3				3	3
2	5.4	69	2	20	2	1					5	
1	6.0	91			4							

TABLE 3

Dye	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
3	9.0	90		5						1.2	5	
6	1.5	85	5	5		0.15	5.0	0.2				
9	2.5	90		6	4					0.12		
10	3.1	82	4	8		0.3						6
11	0.9	85		10					5	0.2		
12	8.0	90		5	5			0.3				
14	4.0	70		10	4				1		4	11
2	2.2	75	4	10	3				2		6	
3	10.0	91			6						3	
5	9.0	76		9	7		3.0			0.95	5	
4	5.0	78	5	11							6	
6	5.4	86			7						7	
8	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
9	2.0	90		10								
10	2	88						10				
13	5	78			5			12			5	
14	8	70	2		8			15			5	
6	10	80						8			12	
1	10	80		10								

CLAIMS

1. A compound of Formula (1) and salts thereof:



Formula (1)

wherein:

B¹ and B²

are each independently -SO₃H, -COOH, -CF₃, optionally substituted alkoxy, optionally substituted alkyl or -PO₃H₂;

Q

is an organic linking group;

R¹ and R²

are each independently H or optionally substituted alkyl;

each A

independently is N, C-Cl, C-CN or C-NO₂;

Z¹ and Z²

are each independently -SR³, -OR⁴, -NR⁵R⁶ or a labile atom or group;

R³, R⁴, R⁵ and R⁶

are each independently H, optionally substituted alkyl, optionally substituted aryl or optionally substituted aralkyl; or

R⁵ and R⁶

together with the nitrogen to which they are attached form an optionally substituted five or six membered ring.

2. A compound according to claim 1 wherein B¹ and B² are attached ortho to the azo group.

3. A compound according to either claim 1 or claim 2 wherein B¹ and B² are sulphonyl.

4. A compound according to any one of the preceding claims wherein Z^1 and Z^2 are each independently $-SR^3$, $-OR^4$ or $-NR^5R^6$ wherein R^3 , R^4 , R^5 and R^6 are as defined in claim 1.

5. A compound according to any one of the previous claims wherein:

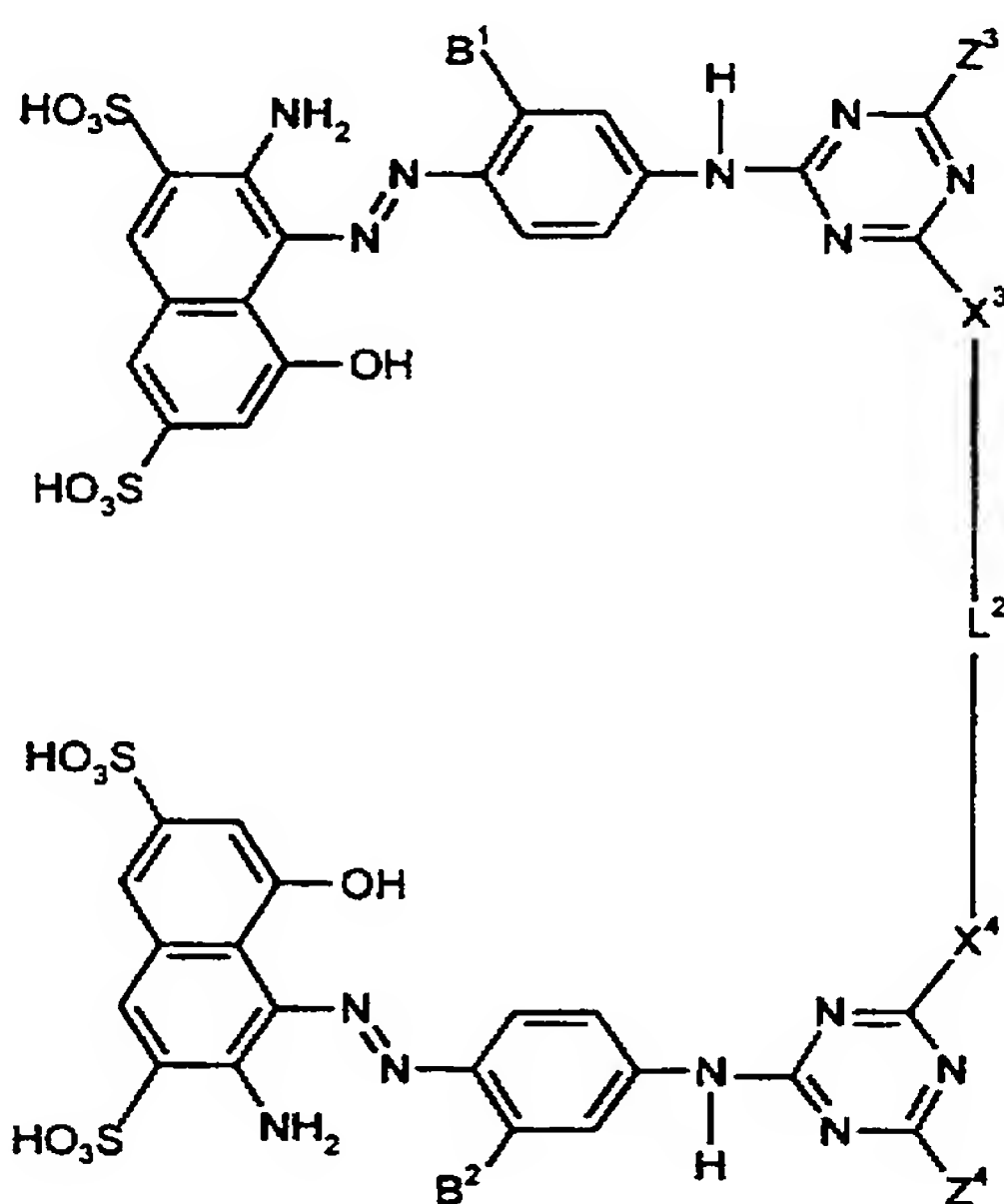
Q is an optionally substituted piperazinylene group, or a group of the formula $-X^1-L-X^2-$;

X^1 and X^2 are each independently an optionally substituted piperazinylene group, $-S-$, $-O-$ or $-NR^7-$;

R^7 is H, optionally substituted alkyl or optionally substituted aryl; and

L is a divalent organic linking group.

6. A compound according to claim 1 of the Formula (5) and salts thereof:



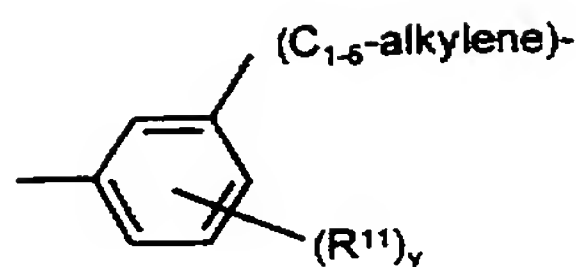
Formula (5)

wherein:

X^3 and X^4 are each independently an optionally substituted piperazinylene group, $-S-$ or a group of formula $-NR^7-$;

R^7 is H, optionally substituted alkyl or optionally substituted aryl;

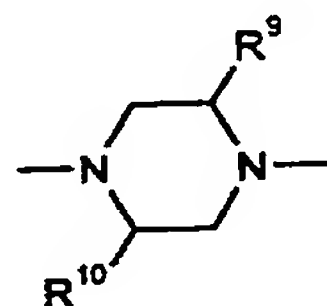
L^2 is optionally substituted phenylene, a group of the Formula (2), or C_{2-6} -alkylene optionally interrupted by $-O-$, $-S-$, phenylene, $-NR^7-$, $-C(O)-$, $-C(O)O-$ or an optionally substituted piperazinylene group:



Formula (2)

each R^{11} independently is H, C_{1-4} -alkoxy, F, Cl, $-SO_3H$, $-COOH$, $-OH$, $-CN$, $-NO_2$,
 5 $-NH_2$ or C_{1-4} -alkyl optionally substituted by hydroxy, carboxy or sulpho;
 y is 1 to 4; or
 $-X^3L^2X^4-$ forms an optionally substituted piperazinylene group;
 Z^3 and Z^4 are each independently Cl, F, $-SR^3$, $-OR^4$ or $-NR^5R^6$; and
 R^3 , R^4 , R^5 , R^6 , B^1 and B^2 are as defined in claim 1.

10 7. A compound according to claim 6 wherein the optionally substituted piperazinylene groups referred to in the definitions of X^3 , X^4 and L^2 are of Formula (3):



Formula (3)

15 wherein:

R^9 and R^{10} each independently is H or C_{1-4} -alkyl optionally substituted by hydroxy, sulpho or carboxy.

20 8. A compound according to either claim 6 or claim 7 wherein:

X^3 and X^4 are each independently $-NR^8-$ or $-S-$;

Z^3 and Z^4 are each independently $-SR^{16}$ or $-NR^{17}R^{18}$;

R^{16} and R^{17} are each independently a group of the formula
 25 $-(C_{1-6}\text{-alkylene})O(C_{1-6}\text{-alkylene})OR^{19}$ or C_{1-6} -alkyl optionally substituted by C_{1-4} -alkoxy, hydroxy, carboxy, sulpho, tetrahydrofuryl, morpholinyl or a group of the formula $-NR^{19}CO(C_{1-4}\text{-alkyl})$;

R^8 , R^{18} and R^{19} are each independently H, C_{1-4} -alkyl or C_{1-4} -hydroxyalkyl;

B^1 and B^2 are sulpho; and

L^2 is as defined in claim 6.

30 9. A compound according to claim 8 wherein L^2 is C_{2-10} -alkylene interrupted by $-NR^8-$ wherein R^8 is as defined in claim 8.

10. A composition comprising one or more compound(s) according to any one of claims 1 to 9 and a medium.

11. A composition according to claim 10 comprising:

- 5 (a) from 0.01 to 30 parts of one or more compound(s) according to any one of claims 1 to 9; and
- (b) from 70 to 99.99 parts of a medium comprising a mixture of water and an organic solvent, an organic solvent free from water, or a low melting point solid;

10 wherein all parts are by weight and the number of parts of (a)+(b)=100.

12. A process for printing an image on a substrate comprising applying thereto an ink containing a compound according to any one of claims 1 to 9 by means of an ink jet printer.

15 13. A process according to claim 12 wherein the ink is a composition according to either claim 10 or claim 11.

20 14. A paper, an overhead projector slide or a textile material printed with a composition according to either claim 10 or claim 11, or by means of the process according to either claim 12 or claim 13.

15. An ink jet printer cartridge containing an ink, characterised in that the ink contains one or more compound(s) according to any one of claims 1 to 9.

25 16. A compound substantially as hereinbefore described with reference to any one of the examples.

30 17. An ink substantially as hereinbefore described with reference to any one of the examples.



Application No: GB 9825225.7
Claims searched: 1-17

Examiner: Stephen Quick
Date of search: 4 March 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q):

Int Cl (Ed.6):

Other: Online: CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0693538 A2 (CIBA-GEIGY), see pages 2 (lines 1-10), 15 (lines 14-20), 21 (substructures M, N, O & P), 24-25 (substructures a-l), 38 (formula), 39ff (examples 113-115, 117 & 119), 45 (formula, line 35), 46 (example 177), 47 (formula, line 50), 49 (examples 192 & 193) and claims 11, 21, 29 & 30	1-11 & 14
&	US 5631352 A (CIBA-GEIGY)	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.